

AN INVESTIGATION OF THE USE OF ODORANTS IN LIQUEFIED NATURAL GAS USED AS A VEHICLE FUEL

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Key Words: Liquefied Natural Gas, LNG Odorization, LNG Vehicles

ABSTRACT

Interest in liquefied natural gas (LNG) as an alternative vehicle fuel has increased significantly. Its greater storage density relative to compressed natural gas makes it an attractive option for both volume and weight constrained vehicle applications. The public transportation market, specifically transit bus properties, have been very aggressive in pursuing LNG as an alternative vehicle fuel. Naturally, when dealing with the general public and a new transportation fuel, the issue of safety must be addressed. With this in mind, the Gas Research Institute has initiated a number of safety related studies including an investigation of the use of odorants in LNG. This paper presents the preliminary results of an investigation performed by the Institute of Gas Technology to determine both the applicability and effectiveness of odorizing LNG. This includes an overview of the current state-of-the-art in LNG vehicle fueling and safety systems as well as a discussion of an LNG odorization program conducted by San Diego Gas & Electric in the mid 70s'. Finally, the paper discusses the results of the modeling effort to determine whether conventional odorants used in natural gas can be injected and remain soluble in LNG at temperatures and pressures encountered in LNG fueling and on-board storage systems.

INTRODUCTION

Interest in LNG vehicles and LNG refueling systems is growing due to the clean burning characteristics of natural gas and the abundant supply of natural gas in North America. As directed by many U. S. codes, natural gas distributed to customers is odorized to the extent that its presence in the atmosphere is readily detectable at gas concentrations of one-fifth of the lower explosive limit. Although LNG is currently not odorized, odorization may provide a significant increase in safety for over the road transportation of LNG and LNG vehicles. Unfortunately, the cryogenic temperature (-260°F) of LNG results in the immediate solidification of any known odorant. Therefore, special odorants and blending techniques must be developed to provide for the proper and effective odorization of LNG.

The objective of this paper is to present potential odorants (or odorant mixtures) and carriers for service in LNG. This includes an evaluation of the concentration of candidate odorants necessary to achieve an acceptable warning level and also the concentration level at which the candidate odorant reaches the solubility limit in LNG and the potential carrier.

SAFETY SPECIFICATIONS

In the United States, detection by odor is typically required before concentrations of natural gas in air reach 1/5th the lower combustible limit of the gas. That is, before natural gas concentration in air reaches 1%. It is implied that a large fraction of the adult population shall recognize the odor when the natural gas is diluted 100 to 1 in air.

Although human response to odors has long been studied, there has been to date little agreement on the theoretical basis for selecting odorants. A widely accepted measure of odorant effectiveness is the "median threshold" level: that concentration in air at which 50% of a test group can consistently detect the presence of the odor without necessarily being able to identify it. "Recognition" level, where 50% of a test group can characterize the odor, is said to be 2 to 5 times the threshold, Kniebes³, but it is not often reported as measured.

More recently, Ripley et al.⁶, introduced the concept of "Warning Level" at which an extrapolation of threshold data to 100% of a population experiencing threshold is the warning level. This definition of warning concentration has its foundation in theory and experiment, and it yields results that compare well with field practice and the data of Ripley. The factor 5 means that most of the population experiences this concentration as very much larger than 5 times their threshold. For t-butyl mercaptan, for example, 50% of the population should experience this odor at a concentration more than 120 times their threshold experience; for thiophane 44 times threshold. Note that the factor 5 is reasonable for odorizing LNG but not where odor fading is likely, i.e., odorizing gas for a transmission or distribution system.

SOLUBILITY

The presence of solids in the flow lines and fittings from an LNG storage tank to an engine can reduce or stop the flow of fuel. Thus, for potential odorants in LNG, it is important to know their solubility limits in LNG, that is, the concentration at which solid odorant begins to precipitate out of solution. A second solubility issue arises in consideration of procedures for introducing odorant into LNG. Because the triple point of candidate odorants are all above the temperatures at which LNG will be stored, the pure

odorants cannot be cooled to LNG temperature prior to placement in LNG. It is useful to consider dissolving the odorant into a carrier liquid and subsequently cooling the carrier/odorant mixture to LNG temperature. The candidate carrier liquids include only Propane and i-Butane.

It is always preferable to have experimental solubility data. In the event such data cannot be found then solubility can be estimated on the following thermodynamic basis. The solid at the triple point of pure material is used as a reference point. The solid is cooled to temperature at which the solubility limit is desired and its fugacity is calculated along this path. The pure liquid is cooled from the triple point to the temperature of interest, then mixed with the LNG: the fugacity of the odorant in solution is calculated along this path. At equilibrium the two fugacities thus calculated must be equal and the limiting concentration in the liquid phase can then be computed.

H = enthalpy	subscripts
F = Gibbs free energy	o - reference state
S = entropy	s - solid
f = fugacity	l - liquid
H _{fusion} = heat of fusion	i - component i
T = absolute temperature	t - temperature
v = volume	p - pressure
C _p = specific heat	
a = activity coefficient	

$$F = H - TS, \quad (dF/dT)_p = -S, \quad (dF/dp)_T = v;$$

For the solid at T

$$S_s = S_o + \int C_{ps} dT / T$$

$$F_i = F_s = F_o - \int (S_o + \int C_{ps} dT / T) dT$$

For the liquid at T

$$S_l = H_{\text{fusion}} / T_t + \int C_{ps} dT / T$$

$$F_l = F_o - \int (S_o + H_{\text{fusion}} / T_t + \int C_{ps} dT / T) dT$$

For the odorant in solution at T

$$F_i = RT \ln(a_i x_i) + F_i = F_s$$

The activity coefficient can be estimated from Scatchard's equation² as discussed by Preston and Prausnitz⁵.

$$\ln(a_i) = v_i V_{fj} ((d_i - d_j)^2 + 2L_{ij} d_i d_j) / RT$$

Here:

- v_i = the molar volume of the odorant at temperature T
- V_{fj} = the volume fraction of the solvent
- d_i and d_j = the solubility parameters of odorant and solvent
- L_{ij} = a parameter characterizing the interaction of i and j
- R = the gas constant in appropriate units.

The solubility parameters are effectively the internal energy change on vaporizing a unit volume of the liquid at 298.16°K and they characterize the cohesive energy density of a chemical. The activity coefficient calculated by this method is very sensitive to the term L_{ij} : a value of 0 leads to maximum solubility, a value 0.08 to a very low solubility. In the absence of experimental data to guide the selection of L_{ij} , it will be important to choose an extreme value, say 0.08, so that the limiting case solubility has been estimated.

Where the integrations cited above are over a relatively small temperature range and vapor/liquid equilibrium data can be used to calculate values for L_{ij} , then it is not necessary to choose the limiting case value. Such data are available for thiophane, t-butyl mercaptan, isopropyl mercaptan, dimethyl sulfide and ethyl mercaptan in vapor/liquid equilibrium with propane.

There are data available for the solubility of t-butyl mercaptan in methane and LNG⁴, but the temperature interval between t-butyl mercaptan's triple point, 274.26°K and LNG temperature, 112°K is such that a useful value of the integrals cited above cannot be adequately evaluated. For its solubility in propane the following limiting case approach was made: For several values of L_{ij} for methane-t butyl mercaptan the integral was evaluated from the product $x_i a_i$ at 112°K with x_i from Reference 4, then the solubility in propane was evaluated with L_{ij} from vapor-liquid equilibrium data. On inspection of results a conservative value of the integral was selected to enable calculation of t-butyl mercaptan solubility in propane adequate for the screening process of this work.

Fortunately, AIChE's data compilation¹ provides up-to-date correlations for the heats of fusion, densities and specific heats of liquid and solid, and solubility parameters of the chemicals of interest here: various odorants, methane and the potential odorant carriers propane and i-butane. Table 1. lists the solubility limits for promising candidate odorants in methane with $L_{ij} = 0.08$ (worst case) with their warning concentrations, both in ppm. It is clear that all are adequately soluble in methane and LNG.

TABLE 1. ODORANT SOLUBILITY AND REQUIRED CONCENTRATIONS IN METHANE

Odorant	Solubility, ppm	Warning Concentration, ppm
Ethyl Mercaptan	3785	0.4
i-Propyl Mercaptan	1746	0.6
n-Propyl Mercaptan	630	1.5
i-Butyl Mercaptan	941	1.0
t-Butyl Mercaptan	68	0.1
Thiophane	5	0.6
Dimethyl Sulfide	419	2.9

Values of L_{ij} can be obtained from vapor-liquid equilibrium data. At the low vapor pressures of the odorants it is enough to have values of $K_i = y_i/x_i$ in a given solvent to get $a_i = P^*K_i/P_i$. Here y_i and x_i are the mole fractions of odorant in the vapor and liquid phases, P is the total pressure and P_i is the vapor pressure of the odorant. The value of L_{ij} thus evaluated at several temperatures should be temperature independent and applicable to estimating the solubilities in the solvent at LNG temperature. The data of Ng and Robinson⁷ were used to evaluate L_{ij} for ethyl, isopropyl and t-butyl mercaptans, and dimethyl sulfide dissolved in propane; Whisman et al. data⁸ for L_{ij} of thiophane in propane. The values of L_{ij} and the solubilities of these compounds in propane are shown in the Table 2.

TABLE 2. ODORANT SOLUBILITY IN PROPANE

Odorant Name	L_{ij}	Solubility limit ppm in Propane
Ethyl Mercaptan	0.032	83700
Isopropyl Mercaptan	0.042	27600
t-Butyl Mercaptan	0.044	736
Dimethyl Sulfide	0.031	7976
Thiophane	0.029	673

Note that the processes for evaluation require estimation of the properties of the subcooled liquid, but experimental data will be available only for saturated liquid. To test the validity of integration of the correlations of specific heat into the subcooled region an alternative extrapolation procedure was used and the two results compared. The alternative was a linear extrapolation from the triple point with the rate of change of C_p with temperature that at the triple point. Integrations from the triple points to 112° K for 9 potential odorants differed, on absolute average less than 0.2%, with the maximum deviation 0.5%. These results show that the extrapolations are justified, and they lend credence to the programming that implements the process of evaluation. Note also that pressures are low and the molar volume of solids and liquids are small. Thus neglecting the integral $(v_s - v_l)dp$ will involve negligible error.

It will be observed that the activity coefficient is a function of odorant concentration so that the solubility limit can not be determined in a single step. In this work it was sufficient to start with the concentration estimated for $a_i=1$ to calculate an initial value for solubility: the value for solubility was used to obtain a new value for a_i which enabled calculation of a new solubility and the process was repeated until changes in solubility were less than 0.02% of the previous value.

In practice it is desirable to use relatively small amounts of carrier, in the range of 1 gallon carrier to 1000 gallons of LNG. These small amounts will not appreciably affect the composition of the liquid methane ($> 99.5\%$ pure CH_4) being used by an increasing number of fleets. The concentration of odorant in carrier can be calculated

$$C_o = C_w * (1 + (D_l/D_c) * R)$$

- C_w = the warning concentration of odorant in LNG at 1/5th LEL
 C_o = concentration of odorant in carrier required to achieve C_w warning concentration in LNG
 D_l/D_c = the ratio of LNG to carrier densities in moles/volume
 R = the ratio gallons LNG/gallon odorant

The symbol * in Table 3. indicates that the required concentration is greater than the solubility limit shown. At the level of 1 gallon per 1000 gallons of LNG n-propyl mercaptan is probably satisfactory because L_{ij} is almost certainly smaller than 0.08, but n-butyl mercaptan and thiophane would require

experimental data to justify their use. The average value of L_{ij} for thiophane reported above represents a wider scatter of individual values than the others and is therefore less adequate as a basis for estimating limiting solubility. Given the possibility of overdosing odorant under field conditions, the table above suggests that the ethyl, i-propyl and t-butyl mercaptans are best suited to odorization of LNG at the propane to LNG volume ratio of 1/1000.

Table 3. ODORANT REQUIREMENTS WITH PROPANE AS CARRIER

Odorant	Cw, ppm	R=1000 Co	Solubility limit, ppm	Lij
Ethyl Mercaptan	0.4	941	83700	0.032
i-Propyl Mercaptan	0.6	1294	27500	0.042
n-propyl Mercaptan	1.5	3528*	1766	0.08
i-Butyl Mercaptan	1.0	2234	2697	0.08
n-Butyl Mercaptan	1.0	2234*	185	0.08
t-Butyl Mercaptan	0.1	235	746	0.044
Dimethyl Sulfide	2.9	6821	7976	0.031
Thiophane	0.6	1411*	673	0.029

To produce a carrier with the desired concentration of odorant, we can assume the mixing process to take place at 25°C (77°F).

$$V_o = (C_o/1000000) \cdot (D_c/D_o) \cdot 28316/7.48$$

V_o = volume of odorant needed, cc odorant/gallon carrier
 C_o = concentration of odorant desired, ppm
 D_c/D_o = ratio of densities in moles/volume, carrier/odorant at 77°F, 28316/7.48 = cc/gallon

Note that, on substitution from the previous relationship between C_o and C_w and taking $1 \ll (D_i/D_o) \cdot R$, we have

$$V_o = C_w \cdot (D_i/D_o) \cdot R \cdot 28316/7.48e6$$

We see that V_o is for practical purposes independent of the density of the carrier, and is thus as applicable for carriers other than propane. As shown in Table 4., 10 gallons of propane containing 11 cc of t-butyl mercaptan would odorize an LNG trailer load of 10,000 gallons.

Table 4. CUBIC CENTIMETERS OF ODORANT PER GALLON OF CARRIER; (PROPANE)

Odorant	<u>V_o, cc/gal. R=1000</u>
Ethyl Mercaptan	3.0
i-Propyl Mercaptan	5.2
n-propyl Mercaptan	13.6
i-Butyl Mercaptan	10.3
n-Butyl Mercaptan	10.2
t-Butyl Mercaptan	1.1
Dimethyl Sulfide	21.2
Thiophane	5.3

ODORANT CONCENTRATION IN EQUILIBRIUM LNG VAPOR

It is clear that all the odorant in LNG will be released to the surroundings if the liquid is totally evaporated. But the odorant concentration of the vapor in equilibrium with LNG liquid or of the vapors leaving an LNG spill are not going to be that of the original LNG. To establish the concentration of odorant in the vapor over LNG liquid the following process was used: Taking the reference states of pure component odorant and methane as 112°K and the vapor pressure of the odorant at 112°K, the equality of fugacities in the liquid and vapor phases can be expressed in terms of mole fractions

$$y_i = a_i \cdot x_i \cdot P_i/P$$

Here:

a_i = the activity coefficient of the odorant
 y_i, x_i = the mole fractions of odorant in the vapor and liquid respectively
 P_i = the vapor pressure of the odorant at T temperature
 P = the pressure of the equilibrium mixture at T

The activity coefficient can be estimated from Scatchard's equation² as discussed by Preston and Prausnitz⁵, and described above. The activity coefficient calculated by this method is very sensitive to the term L_{ij} : a value of 0 leads to the minimum values for a_i and y_i ; a value of 0.08 is extreme, and leads to very high values for a_i and y_i . Use of the value $L_{ij} = 0.08$ therefore leads to an optimistic value for the concentration of odorant in the vapors in equilibrium with LNG. The values of 0.0 and 0.08 were used to screen potentially useful odorants. If, with $L_{ij} = 0.08$, the concentration of odorant is far below the threshold level, then certainly the vapor will not be detected by its odor.

Daubert¹ and Danner's data compilation provides data for the vapor pressures, densities and solubility parameters of methane, ethane, propane and i-butane, and a variety of candidate odorants. Because LNG temperature is well below the triple point of the liquid where the pure odorant exists only as a solid, it is necessary to estimate the vapor pressure of the liquid by extrapolation. Two methods suggest themselves: 1) use the correlation of vapor pressure presented by Daubert and Danner at temperatures below the triple point and 2) assume the form $\ln(P_i) = A/T+B$, and calculate the vapor pressure by evaluating $d\ln(P_i)/dT$ and P_{i0} at the triple point, so that $P_i = P_{i0} \exp((T-T_{i0}) \cdot (d\ln(P_i)/dT))$. To estimate y_i , both values of P_i were calculated and the larger one used in the calculation. Because it is likely that the true values lie between the two, the larger value gives a conservative estimate given that the results are far below the warning level.

With odorant concentration of 5 ppm in methane, $L_{ij} = 0.08$, $T = 112^\circ\text{K}$, and $p = 16$ psig, values of y_i were calculated for 8 odorant candidates with the results shown in Table 6. For all odorants values of y_i are far below that needed to obtain threshold concentrations when mixed with air at 1/5th the lower flammable limit for methane.

TABLE 6. ODORANT CONCENTRATION IN METHANE VAPOR

Odorant	y_i , ppb	P_i , psia	a_i	$K_i = y_i/x_i$
Ethyl Mercaptan	0.000200	3.9e-9	166	4e-8
i-Propyl Mercaptan	0.000043	8.6e-10	158	8.6e-9
n-Propyl Mercaptan	0.000129	8.9e-10	459	2.6e-8
n-Butyl Mercaptan	0.000004	1.0e-11	1203	8.0e-10
i-Butyl Mercaptan	0.000000	1.5e-12	598	-
t-Butyl Mercaptan	8.5	2.6e-4	103	1.7e-3
Dimethyl Sulfide	0.0234	4.0e-7	187	4.7e-6
Thiophane	0.000139	2.2e-11	20000	2.8e-8

All are far below the parts per million levels required for detection by odor. T-butyl mercaptan seems an anomaly in this list, but that is probably because the extrapolation from the triple point, 264.26°K , down to 112°K is so far that the estimate of P_i is much lower than the true value.

Vapor in equilibrium with LNG that is released into the atmosphere will not be detected by its odor: the concentration of odorant is just too small. However, the issue is not closed because the plausible occurrences and magnitude of such releases has not yet been established. Furthermore, LNG droplets or aerosols may emanate from the boiling liquid and become entrained in the escaping gas. To the extent that this may occur, additional odorant may be present in the released vapor.

CONCLUSION & RECOMMENDATIONS FOR ODORANTS & CARRIER

The elimination of some candidate carriers is quite easy: n-butane and the heavier hydrocarbons can be immediately eliminated as carriers because their freezing points are too high. Ethane is not a desirable carrier because its critical temperature, 90.1°F , is within the range of ambient temperatures so that phase densities can radically change with small temperature or pressure changes while mixtures are being made or transferred. Only propane and i-butane are sensible candidates, commercially available and typical components of LNG. Propane is clearly preferable to i-butane because it is more universally available, and its phase equilibrium with odorants has received more experimental attention.

Although 10 mercaptans, hydrogen sulfide, dimethyl sulfide and thiophane were examined during this work, only 3 were found to satisfy the following criteria:

1. There exist adequate experimental data on its odor detection to define the warning concentration of odorant required in LNG. This rules out sec-butyl mercaptan.
2. Concentration of odorant in propane carrier, with Carrier/LNG ratio 1/1000, is well below the solubility limit with the warning concentration delivered to the LNG. Note that the warning concentration for most odorants is well below their solubility in LNG. This rules out thiophane.
3. At the propane/LNG ratio of 1/1000, any plausible overdose of odorant during mixing of odorant with propane will not lead to formation of solids when the result is cooled to LNG temperatures. This rules out all but the ethyl, i-propyl and t-butyl mercaptans on the basis of the experimental data available at present.

4. The odorant is not identified as acutely toxic by EPA - this rules out methyl mercaptan and dimethyl sulfide.
5. The odor in air is perceived as "gassy". This rules out dimethyl sulfide.

The acceptable candidate odorants are:

Ethyl Mercaptan
i-Propyl Mercaptan
t-Butyl Mercaptan

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